

Synthesis of ammonia directly from wet air at intermediate temperature

Rong Lan, Khaled A. Alkhazmi, Ibrahim A. Amar, Shanwen Tao*

Department of Chemical & Process Engineering, University of Strathclyde, Glasgow G1 1XJ, UK

ARTICLE INFO

Article history:

Received 3 December 2013

Received in revised form 4 January 2014

Accepted 20 January 2014

Available online 27 January 2014

Keywords:

Ammonia

Synthesis

Air

Water

Intermediate temperature

ABSTRACT

For the first time, ammonia has been directly synthesised from wet air at intermediate temperature. $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ (CCO)– $(\text{Li},\text{Na},\text{K})_2\text{CO}_3$ electrolyte together with a new perovskite oxide $\text{Pr}_{0.6}\text{Ba}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ were used for electrochemical synthesis of ammonia. An ammonia formation rate of $1.07 \times 10^{-6} \text{ mol s}^{-1} \text{ m}^{-2}$ was obtained at 400°C when applied a voltage of 1.4 V, while wet air was introduced to the single chamber reactor. This is just slightly lower than the value of $1.83 \times 10^{-6} \text{ mol s}^{-1} \text{ m}^{-2}$ when wet N_2 was fed under the same experimental conditions. These values are two to three orders of magnitude higher than the reported ammonia formation rates when synthesised from N_2 and H_2O at $\sim 600^\circ\text{C}$. The perovskite catalysts are also low cost compared to the Ru/MgO and Pt/C catalysts in previous reports.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Nitrogen fertiliser has supported approximately 27% of the world's population over the last century, equivalent to around 4 billion people born (or 42% of the estimated total births) since 1908 [1]. Although over 78% of the atmosphere is composed of nitrogen, it is difficult to use N_2 directly by plants as plants can only use fixed nitrogen. The breakthrough in nitrogen fixation took place a century ago, the well-known Haber–Bosch process, operating at high temperature ($\sim 500^\circ\text{C}$) and high pressure (150–300 bar) [2]. Fritz Haber and Carl Bosch won Nobel prize in chemistry in 1918 and 1931 respectively for their contributions in industrial production of ammonia.

In the Haber–Bosch process, the required hydrogen is produced through the steam reforming of natural gas or coal and consumed more than 1% of world power generation [3]. In addition, 1.87 tons of CO_2 is released per ton of ammonia produced [4]. Globally 131 million tons of ammonia was produced in 2010 [5], 245 million tons of CO_2 was released from ammonia industry which is equivalent to 0.77% of the world total CO_2 emission (31.78 billion tons) in 2010 [6]. In order to reduce the current dependency on the fossil fuels and to reduce carbon emissions associated with their use, it is essential to introduce new ammonia synthesis process and break the link between fossil fuels and ammonia industry [7]. The electrochemical synthesis processes are among the promising

alternatives in particular if the hydrogen required for ammonia synthesis is produced from non fossil fuel resources [2,8–11]. Recently, it has been reported that ammonia can be directly synthesised from air and water at ambient conditions, bypassing the N_2 separation and hydrogen production stage [2]. In a recent experiment, it was found that ammonia formation rates were even higher at 80°C than those at room temperature which means reasonably higher working temperature facilitates the ammonia formation [3]. Thermodynamic analysis shows that the equilibrium conversion of ammonia decreases with temperature. Therefore, the higher the temperature, the higher the extent of ammonia decomposition [2]. However, it has been widely reported that ammonia can be synthesised at a temperature as high as $\sim 600^\circ\text{C}$ [8,10,12–15]. The possible reason is that, the decomposition of ammonia at high temperature is kinetically slow thus ammonia can still be collected if it is removed from the reactor in time. Synthesis of ammonia directly from air and water at elevated temperatures would be possible if the oxidation of ammonia is also slow. In this paper, for the first time, we report the synthesis of ammonia directly from wet air at 400°C and ambient pressure. For comparison, ammonia was also synthesised from wet N_2 under the same conditions. Double chamber reactors were previously used for electrochemical synthesis of ammonia from N_2 and H_2O [10] or air and H_2O [2,3]. In this study, a simple single chamber reactor was used to simplify the synthesis process.

In our previous papers, we reported electrochemical synthesis of ammonia from N_2 and H_2 using $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ – $(\text{Li},\text{Na},\text{K})_2\text{CO}_3$ composite electrolyte. $(\text{Li},\text{Na},\text{K})_2\text{CO}_3$ ternary molten salts have an eutectic point of 396°C [16,17]. The low melting point of

* Corresponding author. Tel.: +44 (0) 141 548 2361; fax: +44 (0) 141 548 2539.

E-mail address: shanwen.tao@strath.ac.uk (S. Tao).

mixed $(\text{Li},\text{Na},\text{K})_2\text{CO}_3$ salts makes the composite to exhibit high ionic conductivity at relatively low temperature which can minimise the operating temperature of the cell, reducing the potential thermal decomposition of ammonia. It has been reported that the ionic conductivity of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}-(\text{Li},\text{Na},\text{K})_2\text{CO}_3$ composite reached 0.1 S/cm at a temperature around 400°C [18]. The total ionic conductivity composed those from Li^+ , Na^+ , K^+ , H^+ , HCO_3^- , CO_3^{2-} and O^{2-} ions. Good fuel cell performance based on $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}-(\text{Li},\text{Na},\text{K})_2\text{CO}_3$ composite electrolyte indicates high H^+/O^{2-} ionic conductivity in this type of composite materials [18–21]. Either H^+ or O^{2-} ionic conduction can be used for electrochemical synthesis of ammonia [22]. Therefore a similar composite electrolyte $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}-(\text{Li},\text{Na},\text{K})_2\text{CO}_3$ was used as electrolyte in this study. As for electrocatalysts, ammonia was successfully synthesised using Fe-containing perovskite oxide $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ [14]. Barium is a well known catalytic promoter for ammonia synthesis catalysts therefore strontium was replaced by barium in the new perovskite [23]. Lanthanum was also replaced by multi-valent praseodymium to improve the electronic conductivity. Therefore a new perovskite $\text{Pr}_{0.6}\text{Ba}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ (PBFCu) was synthesised as electro-catalyst for synthesis of ammonia from air/ N_2 and water. $\text{Pr}_{0.6}\text{Ba}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ was used as both cathode and anode and a single chamber reaction was used for the synthesis. The concept for synthesis of ammonia directly from wet air at intermediate temperature has been successfully demonstrated.

2. Experimental

2.1. Materials synthesis

For synthesis of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$, calculated amounts of Gd_2O_3 was dissolved in hot dilute nitric acid to form gadolinium nitrate aqueous solution. Then an appropriate amount of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was added into the solution. $1 \text{ M } (\text{NH}_4)_2\text{CO}_3$ solution was slowly added dropwise with vigorous stirring until pH value reached 7–8, after that vigorous stirring was continued for another 30 min. The formed precipitate was then collected by vacuum filtration and washed several times with deionised water then dried at 100°C overnight. The obtained powder was calcined in air at 650°C for 2 h to obtain ultrafine CGO powder.

$\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ and ternary carbonate mixture $(\text{Li},\text{Na},\text{K})_2\text{CO}_3$ (32.1 wt% Li_2CO_3 ; 34.5 wt% K_2CO_3 ; 33.4 wt% Na_2CO_3) powders were mixed together with weight ratio of oxide to carbonate 7:3. The mixture was put in ball miller (Planetary Mono Mill Pulverisette 6) for mixing with speed of 400 rpm for 4 h. The ball-milled powder was then heated at 600°C for 1 h.

For synthesis of $\text{Pr}_{0.6}\text{Ba}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$, praseodymium oxide (Pr_6O_{11}) was dissolved in diluted nitric acid to form praseodymium nitrate under heating and stirring. Calculated amounts of nitrates $\text{Ba}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_3 \cdot 2.5\text{H}_2\text{O}$ were dissolved in deionised water and were added to the above prepared solution. Appropriate amounts of citric acid and EDTA (ethylenediaminetetraacetic acid) were then added as complexing agents with a molar ratio of citric acid:EDTA:metal cations of 1.5:1:1. Dilute aqueous ammonia solution was then added to the mixed solution to adjust the pH value to around 6. By further heating and calcined in air at 900°C for 2 h, single phase $\text{Pr}_{0.6}\text{Ba}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ was obtained.

2.2. Materials characterisation

TG/DSC analyses were performed using a Stanton Redcroft STA/TGH series STA 1500 operating through a Rheometric Scientific system interface controlled by the software RSI Orchestrator in flowing air at a flow rate of 50 ml min^{-1} .

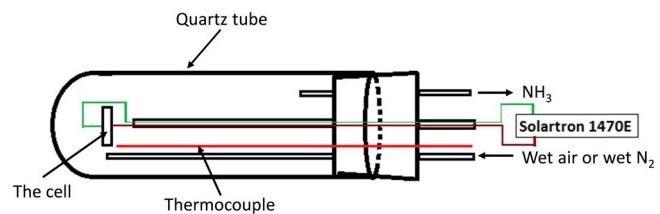


Fig. 1. Schematic diagram of the single chamber reactor used for ammonia synthesis.

X-ray data were collected on a PANalytical X'Pert Pro in the Bragg–Brentano reflection geometry with a Ni-filtered $\text{Cu K}\alpha$ source (1.5405 \AA), fitted with a X'Celerator detector and an Empyrean CuLFF XRD tube. Absolute scans in the 2θ range of 5 – 100° with step sizes of 0.0167° were used during data collection.

Conductivity measurements were carried out by a pseudo-four-terminal method using a computer-controlled Solartron Analytical® SI 1470E electrochemical interface by applying a constant current. The $\text{Pr}_{0.6}\text{Ba}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ powder fired at 900°C was pressed into pellets with diameter of 13 mm and thickness of around 2 mm then fired at 1100°C for 5 h. A silver coated pellet was fitted into the measuring apparatus and measurement was carried out in ambient air.

2.3. Fabrication of the single cell

The cell for ammonia synthesis was a tri-layer single cell which fabricated by a cost-effective one-step dry-pressing and co-firing process. The anode and cathode material was $0.8 \text{ g } \text{Pr}_{0.6}\text{Ba}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ plus 0.2 g composite electrolyte to form a composite electrode materials. The composite anode, composite electrolyte and composite cathode (PBFCu/CGO– $(\text{Li},\text{Na},\text{K})_2\text{CO}_3$ /PBFCu) were fed into the die, layer by layer, with the aid of a sieve to ensure uniform powder distribution, and then uniaxially pressed at pressure of 300 MPa by cold pressing into 13 mm pellets. The pellets were sintered at 600°C for 2 h. The thickness of the anode, electrolyte and cathode was approximately 0.6, 1.0 and 0.6 mm respectively. The catalyst surface area of the cathode and anode was 1.281 cm^2 . Silver paste was painted on each electrode surface of the cell as a current collector. Ag wires were used as output terminals for both electrodes.

2.4. Ammonia synthesis and measurement

The as-prepared cell was put inside a quartz tube sealed by a rubber bung at the cold end. The schematic diagram of the single chamber reactor used for ammonia synthesis is shown in Fig. 1. Compressed air or N_2 was passing through room temperature water before imputing to the single chamber reactor. The flow rate of air (or N_2) was 50 ml min^{-1} . The steam concentration in air (or N_2) was 3 mol%. A dc voltage was applied to the cell using a Solartron 1287E electrochemical interface. The synthesised ammonia was absorbed by 25 ml of diluted sulphuric acid (0.001 M) for 60 min as described before [2,14]. The concentration of NH_4^+ in the absorbed solution was analysed using Orion Application solution for low adjusting ISA. The produced ammonia was detected using an ammonia meter (ISE Thermo Scientific Orion Star A214) and the rate of ammonia formation was calculated using the following equation [2].

$$r_{\text{NH}_3} = \frac{[\text{NH}_4^+] \times V}{t \times A} \quad (1)$$

where $[\text{NH}_4^+]$ is the measured NH_4^+ ion concentration, V is the volume of the dilute H_2SO_4 for ammonia collection, t is the adsorption time, A is the effective area of the cell.

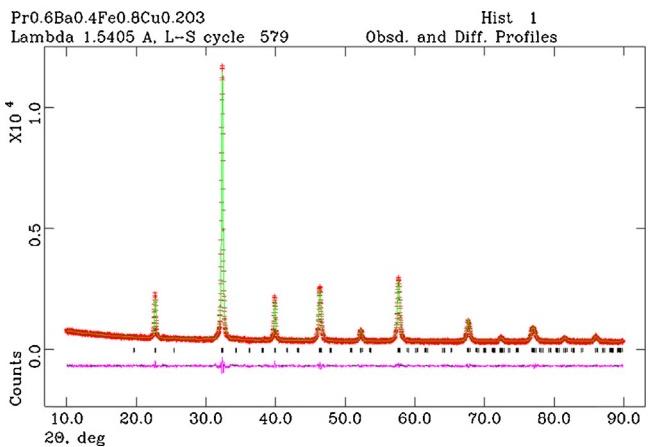


Fig. 2. XRD pattern of $\text{Pr}_{0.6}\text{Ba}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ at room temperature.

3. Results and discussion

3.1. Structure and conductivity of $\text{Pr}_{0.6}\text{Ba}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$

As for preparation of $\text{Pr}_{0.6}\text{Ba}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$, STA analysis of ash indicates the reaction completes at a temperature around 820 °C (Fig. 4A) therefore a firing temperature of 900 °C has been chosen (Fig. 3A). XRD analysis of the powder after firing at 900 °C indicates it is a single phase (Fig. 2). It exhibits an orthorhombic structure with space group Pnma(62); $a = 5.5447(6)$ Å, $b = 7.8070(3)$ Å, $c = 5.5397(6)$ Å, $V = 239.80(4)$ Å³ (Table 1). In our previous report, perovskite oxide $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ exhibits a cubic structure with space group Pm-3m (221). The ionic size of Ba^{2+} ions (1.61 Å) is much larger than that for Sr^{2+} ions (1.44 Å) at coordination number of 12 but ionic size of Pr^{n+} ($n = 3, 4$) is just slightly smaller than La^{3+} ions [24]. When Sr^{2+} ions are replaced by larger Ba^{2+} ions, lattice distortion becomes significant resulting in lower symmetry. Perovskite oxides PrFeO_3 and $\text{Pr}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ also exhibit orthorhombic structure with space group Pnma(62) [25]. It was reported that perovskite oxide PrBaCuFeO_{5+y} exhibits the ordering of both A- and B-sites with a space group P4/mmm(123). This is a tetragonal structure with $a = a_p$, $c = 2a_p$ where $a_p \approx 4$ Å, in which a_p is the lattice parameter of primitive cubic structure. The possible A-site ordering of Pr^{3+} and Ba^{2+} ions was not observed in $\text{Pr}_{0.6}\text{Ba}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ as A-site ordering will lead to cubic or tetragonal structure [26]. The lattice parameters a and b in $\text{Pr}_{0.6}\text{Ba}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ are significantly different indicating it is orthorhombic rather than tetragonal structure. Therefore $\text{Pr}_{0.6}\text{Ba}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ exhibits an orthorhombic structure without cation ordering.

The electronic conductivity of $\text{Pr}_{0.6}\text{Ba}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ is very important in order to be used as both cathode and anode for the electrochemical cells for ammonia synthesis. Dc conductivity measurement indicated that the conductivity increased before 425 °C, reached a value of 5.25 S/cm then started to decrease (Fig. 3). This is probably due to the semi-conductor to metal transition which is a common phenomenon in perovskite oxides [27]. Thermal analysis of $\text{Pr}_{0.6}\text{Ba}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ in air indicated the gradual loss of oxygen at a temperature above 350 °C (Fig. 3B). The semiconductor to metal transition could be related to the loss of oxygen. No obvious thermal effect was observed on the DSC curve indicates $\text{Pr}_{0.6}\text{Ba}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ does not exhibit first order phase transition up to measured 800 °C (Fig. 4B). As for the operating temperature of the cell, the lowest working temperature of the CGO-(Li,Na,K)₂CO₃ composite electrolyte is 400 °C, very close to the highest conductivity of $\text{Pr}_{0.6}\text{Ba}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$. To minimise potential thermal decomposition and oxidation of ammonia,

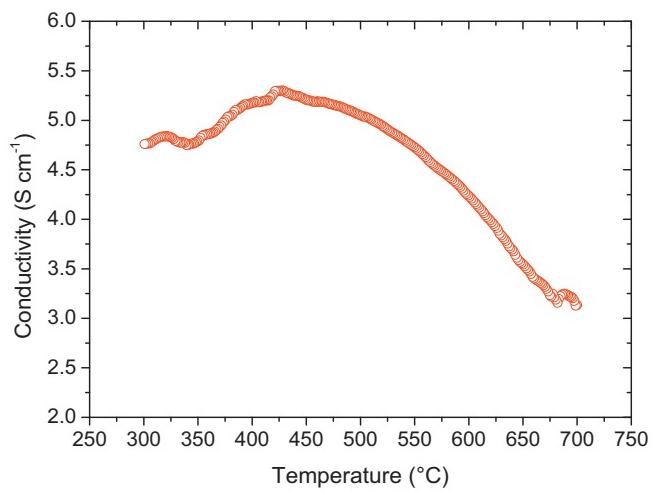


Fig. 3. The dc conductivity of $\text{Pr}_{0.6}\text{Ba}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ in air.

400 °C has been selected as the operating temperature of the cell. In terms of the stability of the (Li,Na,K)₂CO₃ molten salts, it has been reported that the (Li,Na,K)₂CO₃ carbonates is stable in air up to 530 °C [17]. Therefore an operating temperature above 530 °C should be avoided.

3.2. Synthesis of ammonia directly from wet air

As for the first step, wet air was used as the precursor for ammonia synthesis. Compressed air was passing through room

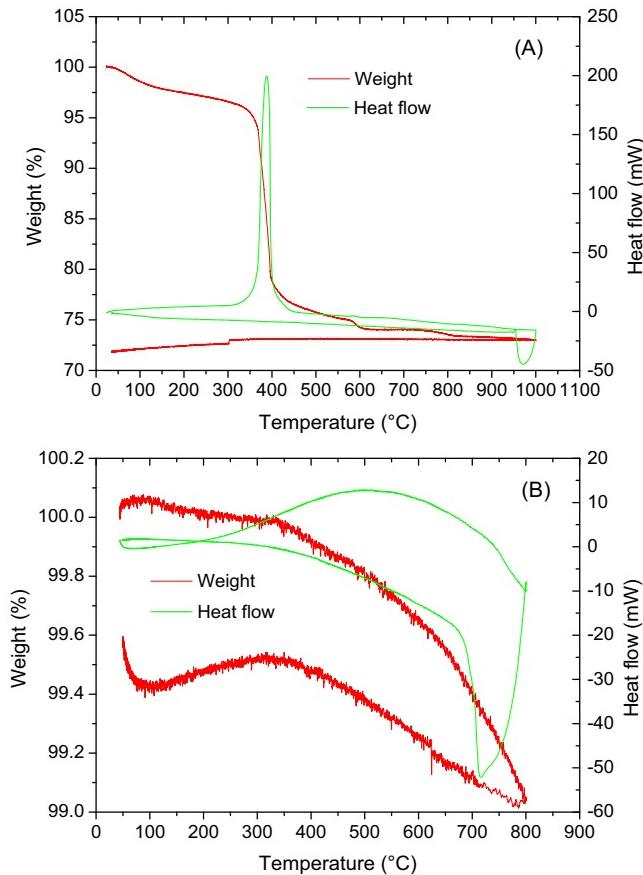


Fig. 4. The STA curves of the $\text{Pr}_{0.6}\text{Ba}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ ash (A) and oxide powder (B) in air.

Table 1Structure parameters of $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$.

Atom	Site	Occupancy	x	y	z	$U_{\text{iso}}/\text{\AA}^2$
Pr	4c	0.6	0.0078(7)	0.25	0.9947(23)	0.0180(4)
Ba	4c	0.4	0.0078(7)	0.25	0.9947(23)	0.0180(4)
Fe	4b	0.8	0.5	0	0	0.0165(6)
Cu	4b	0.2	0.5	0	0	0.0165(6)
O1	4c	1	0.485(6)	0.25	0.053(5)	0.008(9)
O2	8d	1	0.277(6)	0.243(3)	0.733(7)	0.039(5)

Note: Space group Pnma (62); $a = 5.5447(6)\text{\AA}$, $b = 7.8070(3)\text{\AA}$, $c = 5.5397(6)\text{\AA}$, $V = 239.80(4)\text{\AA}^3$, $R_{\text{wp}} = 3.94\%$, $R_{\text{p}} = 3.74\%$, $\chi^2_{\text{red}} = 1.43$.

temperature water before feeding into the single chamber reactor. The gas composition was approximately 3 mol% H_2O , 97 mol% air. The effect of the applied potential on ammonia formation rate was investigated at 400°C and the order for applied voltage was from low to high, between 1.2 and 1.7 V with 0.1 V interval. Fig. 5A shows the recorded current change against time for electrolytic cell during the ammonia synthesis process at different potentials at 400°C over a period of 1 h. As can be seen, at lower applied voltages, the current tends to decrease. The electrolytic cell demonstrated good stability under applied voltage between 1.4–1.6 V. Furthermore, it was found that the current density decreases with increasing applied potential. These could be related to the ‘blocking effect’ of ions as observed in a previous study [3]. As mentioned above, in theory, Li^+ , Na^+ , K^+ , H^+ , HCO_3^- , CO_3^{2-} and O_2^- ions are all mobile in the CGO–($\text{Li},\text{Na},\text{K}$) CO_3 composite electrolyte. When a dc voltage

is applied, the cations tends to move to the cathode while anions tends to move to the anode. As the Li^+ , Na^+ , K^+ ions are blocked by the electrodes; this will form a positively charged layer on the electrolyte side of the cathode/electrolyte interface. HCO_3^- , CO_3^{2-} ions could be partially blocked. Accordingly, a negatively charged layer will be formed on the electrolyte side of the anode/electrolyte interface. The charged layer at the electrode/electrolyte interfaces may block the transfer of H^+ or O_2^- ions leading to reduced current density. Therefore, the current density gradually decreased when a dc voltage was applied. As the first measurement was carried out at 1.2 V, therefore the blocking effect was most significant. The higher the applied voltage, the more significant blocking effect is expected. Therefore, the current density may decrease at higher applied voltage. Following the ion blocking effects observed in the electrochemical cell using $\text{Li}^+/\text{H}^+/\text{NH}_4^+$ mixed conducting electrolyte at 20 and 40°C [3], similar effects was observed at 400°C when CGO–($\text{Li},\text{Na},\text{K}$) CO_3 composite electrolyte was used for electrochemical synthesis of ammonia.

Ammonia was successfully synthesised directly from wet air at 400°C and atmospheric pressure. As can be seen in Fig. 6A the ammonia formation rate increased significantly with the increased applied potential and reached a maximum value at 1.4 V ($1.07 \times 10^{-6}\text{ mol s}^{-1}\text{ m}^{-2}$ at 400°C), showing that 1.4 V was the optimum potential for ammonia synthesis in this study. The same tendency was observed for both wet air and wet N_2 . This could be attributed to nitrogen chemisorption hindered by the high rate of electrochemically supplied H^+ , which in turn poisoned the catalyst (cathode surface) [22,28].

In terms of catalyst weight, the ammonia formation rate was $1.72 \times 10^{-10}\text{ mol s g}_{\text{cat}}^{-1}$. This is more than two orders of magnitudes higher than the reported ammonia formation rates (around $1.0 \times 10^{-12}\text{ mol s g}_{\text{cat}}^{-1}$ at $\sim 600^\circ\text{C}$) when either a H^+ ($\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$) or O_2^- (8 mol% yttria-stabilized zirconia) conducting was used electrolyte, an industrial Ru/MgO catalyst was used at the cathode [10]. The difference is possibly due to the operating temperature, while it was 400°C in our experiment which is roughly 200°C lower than that reported by Skodra and Stoukides [10]. Higher working temperature may cause the thermal decomposition of ammonia.

3.3. Synthesis of ammonia directly from wet N_2

For comparison, ammonia synthesis was also carried out on the same cell using wet nitrogen as the precursor. Fig. 5B shows the recorded current change against time for electrolytic cell during the ammonia synthesis process at different potentials at 400°C . As can be seen, the electrolytic cell demonstrated reasonably good stability under applied voltages. In addition, at the higher voltage (1.7 V), the current is relatively stable but also low amount at the all period of time.

As expected, ammonia was also successfully synthesises directly from wet N_2 at 400°C under atmospheric pressure (Fig. 5A). Again the effect of the applied potential on ammonia formation rate was investigated at 400°C and the order for applied voltage was from

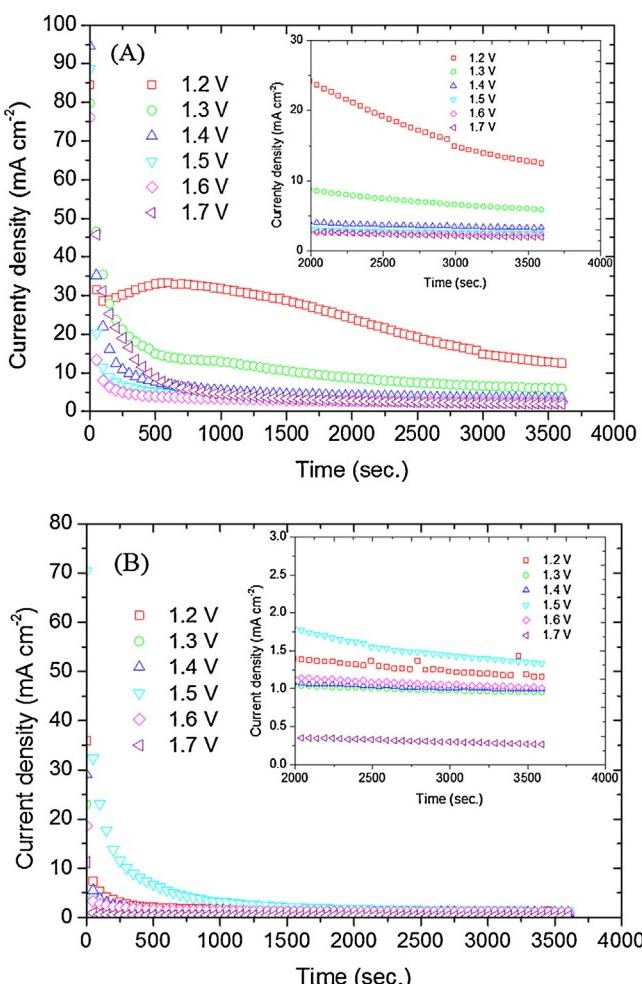


Fig. 5. The current density across the cell in wet air (A) and wet N_2 (B) when applied with different voltages.

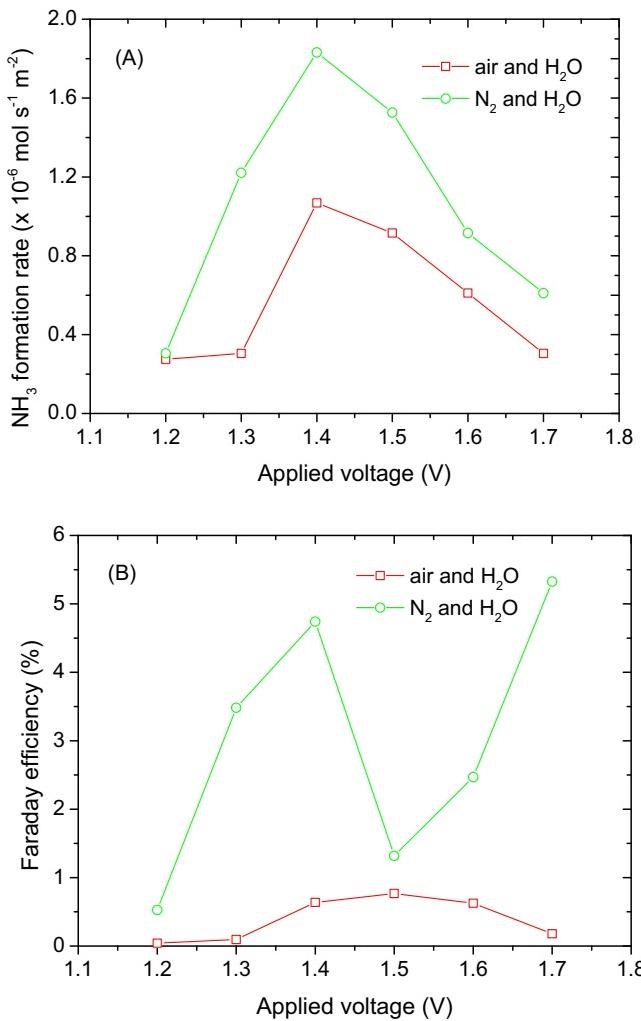


Fig. 6. The ammonia formation rate (A) and Faraday efficiency (B) at 400 °C in wet air and wet N₂ when applied with different voltages.

low to high. The ammonia formation rate increased significantly with the increased applied voltage and reached a maximum value at 1.4 V ($1.83 \times 10^{-6} \text{ mol s}^{-1} \text{ m}^{-2}$ at 400 °C), showing that 1.4 V was the optimum voltage for ammonia synthesis in this study. The rate of ammonia decreased gradually by further increasing of the applied voltage. At 400 °C and 1.4 V, the ammonia formation rates when feeding with wet N₂ was higher than that with wet air. The lower ammonia formation rates when wet air was used could be related to the following reasons: (a) the partial pressure of N₂ in air is lower than that in wet N₂; (b) the presence of O₂ in air may negatively affect the ammonia formation; (c) The formed ammonia is partially oxidized by O₂ in air. Partial oxidation of formed ammonia cannot be ruled out. To further reduce the operating temperature may be beneficial.

In terms of catalyst weight, the ammonia formation rate was $2.93 \times 10^{-10} \text{ mol/s g}_{\text{cat}}$ which is more than 2 orders of magnitude higher than the values reported by Skodra and Stoukides [10]. When applied 1.2 V, the ammonia formation rates for wet air and wet N₂ are comparable (Fig. 5) while more ammonia was produced at higher voltages when wet N₂ was introduced into the single chamber reactor. The Pr_{0.6}Ba_{0.4}Fe_{0.8}Cu_{0.2}O_{3-δ} catalyst used in this study is much cheaper than the Ru/MgO catalyst reported by Skodra and Stoukides [10] and, the Pt/C catalyst used for low temperature synthesis of ammonia [2,3].

4. Discussion

The key finding from our experiments is that, ammonia can be synthesised directly from wet air at intermediate temperature. When a single chamber reactor is used, the key to obtain ammonia from the electrochemical cell is to avoid the possible thermal decomposition and oxidation of ammonia. Although thermodynamically ammonia may decompose to N₂ and H₂ according to reaction (2) at a temperature above 175 °C when the partial pressure of all the gases is 1 bar [2], the real thermo-decomposition temperature is much higher, roughly around 500 °C [29] which makes it possible to synthesise ammonia at a temperature below 500 °C. The possible reason is that, thermo-decomposition of ammonia is kinetically slow. It has been reported that, even at a temperature of 827 °C, short reaction time prevents large decomposition of NH₃ through a homogeneous reaction [30]. At a lower temperature, ammonia decomposition could be minimised if it is removed from the reactor in time.



As for ammonia oxidation at high temperatures, the normal products are N₂ at $T < 800$ K and NO at $T > 800$ K [31].



The oxidation of ammonia in the presence of supercritical water is quite slow at low temperatures. Without a catalyst, at 24.6 MPa, conversion for ammonia oxidation was only 3.4% at 640 °C when the residence time was 11.8 s [32]. At lower temperatures, with absence of ammonia oxidation catalyst, the oxidation of ammonia could be negligible [32].

The slow kinetic processes on decomposition and oxidation of ammonia make it possible to synthesise ammonia directly from wet air. Compared to wet N₂, the N₂ separation from air stage is not required which may save costing on energy and separation device. This will make the synthesis process simpler and more efficient.

As mentioned in previous report, ammonia production is completing with hydrogen production when water was used as a precursor [2]. If the proton conduction of the CGO-(Li,Na,K)₂CO₃ electrolyte was utilised for the electrochemical reactions, then, at the anode:



At the cathode, H⁺ ions may combine with N₂ in air to form NH₃,



The H⁺ ions at cathode can also receive electrons and produce H₂ instead of NH₃,



Reactions (5) and (6) are in parallel and competing with each other. A good catalysts should be in favour of ammonia formation and suppress the H₂ production.

If the O²⁻ ionic conduction of CGO-(Li,Na,K)₂CO₃ electrolyte is used, then the half-cell reaction at the cathode is:



At the anode, O²⁻ ions release electrons and form O₂,



However, water splitting reaction may also happen at the cathode,



Under the circumstance, H₂ instead of NH₃ will be produced.

Therefore, no matter either H^+ or O^{2-} conduction of the CGO–(Li_xNa_yK_z)₂CO₃ composite electrolyte is used for the electrochemical reactions, productions of NH₃ and H₂ are always completing with each other. This ends up with high requirements on the electrochemical catalysts. A good catalyst must meet the following standards: it must be a good ammonia synthesis catalyst and, at the same time, a poor catalyst for hydrogen production, ammonia thermal decomposition and ammonia oxidation. Fortunately, it has been observed that the optimal catalyst for ammonia synthesis is never the optimal catalyst for ammonia decomposition [33]. This makes it possible to identify good ammonia synthesise catalysts while not worry too much on the ammonia decomposition under the same conditions.

Based on the amounts of synthesised ammonia, the Faraday efficiencies of the electrochemical synthesis process under different conditions are also calculated. As shown in Fig. 5B, when wet air was used, the highest Faraday efficiency was 0.77% when a voltage of 1.5 V was applied. In the case of wet N₂, the highest Faraday efficiency was 5.33% at a voltage of 1.7 V. Considering both the ammonia formation rates and Faraday efficiency, an applied voltage of 1.4 V is ideal for both wet air and wet N₂.

The Faraday efficiency for ammonia synthesis was not high when wet air was used as the precursor. Only a small amount of the supplied electricity was used for ammonia production according to reactions (5) or/and (7) while the major part of was used for hydrogen production according to reactions (6) or/and (9).

The circulating of H₂ or O₂ across the cell may cause the decrease in Faraday efficiency as well. When wet air was used, theoretically the O₂ in the air may be pumped from anode to the cathode (oxygen pumping effect), the current used for pump of oxygen is wasted and has no contribution to the production of NH₃ or H₂. From this point of view, to use a proton-conducting electrolyte for ammonia synthesis directly from wet air is a better choice. The hydrogen produced in the electrochemical process will be brought out from the reactor then will not be circulated. This also explains why the Faraday efficiency for ammonia production is much higher when wet N₂ was used. In general, the current density is higher when wet air instead of wet N₂ was fed in the reactor (Fig. 5). This could be related to the high O²⁻ conductivity in the CGO–(Li_xNa_yK_z)₂CO₃ composite electrolyte. In wet N₂, due to the lack of O₂, the current contributed from migration of O²⁻ ions will be significantly lower, leading to lower current density. The absence of O₂ minimised the oxygen pumping effects, particularly the O²⁻ ionic conductivity of CGO–(Li_xNa_yK_z)₂CO₃ is pretty high at the operating temperature. It is expected that this oxygen pumping effect will be minimised if a proton-conducting (instead of O²⁻ ionic conducting) electrolyte is used then higher Faraday efficiency will be achievable.

The typical equilibrium conversion is in the range of 10–15% for the Haber–Bosch process when operating at 430–480 °C [8,34]. When wet N₂ was used, the efficiency is fairly close to that of the Haber–Bosch process. Although the Faraday efficiencies in our experiments are lower than the high efficiency of 78% when H₂ and N₂ was used as the precursor [8], but steam instead of H₂ was used as the precursor in this study, by-passing the hydrogen production and N₂ separation stages.

5. Conclusion

In conclusion, after our previous reports on ammonia synthesis from air and water at ambient temperature and up to 80 °C [6,13], for the first time, ammonia was synthesised directly from wet air at

intermediate temperature (400 °C) using Pr_{0.6}Ba_{0.4}Fe_{0.8}Cu_{0.2}O_{3-δ} as both anode and cathode catalysts. The maximum ammonia formation rate using wet N₂ (1.83×10^{-6} mol s⁻¹ m⁻² at 400 °C) was better than the maximum rate of ammonia production using wet air (1.07×10^{-6} mol s⁻¹ m⁻² at 400 °C). After normalised by the weight of catalysts used, the values are two to three orders of magnitude higher than the reported ammonia formation rates when synthesised from N₂ and H₂O at 600 °C [10]. Our perovskite catalysts are also low cost compared to the Ru/MgO catalysts in previous report [10]. As the ammonia formation rate for wet air still slightly lower than that for wet N₂ indicating partial oxidation. In future, it is necessary to synthesise ammonia at a temperature lower than 400 °C; however, to identify a good proton-conducting electrolyte at this temperature range, also with good chemical compatibility with basic ammonia will be a challenge.

Acknowledgement

The authors thank EPSRC SuperGen XIV 'Delivery of Sustainable Hydrogen' project (Grant No EP/G01244X/1) for funding.

References

- [1] J.W. Erisman, M.A. Sutton, J. Galloway, Z. Klimont, W. Winiwarter, *Nat. Geosci.* 1 (2008) 636–639.
- [2] R. Lan, J.T. Irvine, S.W. Tao, *Sci. Rep.* 3 (2013) 1145.
- [3] R. Lan, S.W. Tao, *RSC Adv.* 3 (2013) 18016–18021.
- [4] <http://www.kbr.com/Newsroom/Publications/Articles/Carbon-Dioxide-Capture-and-Storage-in-the-Nitrogen-Syngas-Industries.pdf> (access 3rd January 2014).
- [5] http://en.wikipedia.org/wiki/Ammonia_production (access 3rd January 2014).
- [6] <http://www.theguardian.com/environment/datablog/2012/jun/21/world-carbon-emissions-league-table-country> (access 3rd January 2014).
- [7] R. Lan, J.T.S. Irvine, S.W. Tao, *Int. J. Hydrogen Energy* 37 (2012) 1482–1494.
- [8] G. Marnellos, M. Stoukides, *Science* 282 (1998) 98–100.
- [9] T. Murakami, T. Nohira, T. Goto, Y.H. Ogata, Y. Ito, *Electrochim. Acta* 50 (2005) 5423–5426.
- [10] A. Skodra, M. Stoukides, *Solid State Ionics* 180 (2009) 1332–1336.
- [11] R. Lan, J.T.S. Irvine, S.W. Tao, *Int. J. Hydrogen Energy* 37 (2011) 1482–1494.
- [12] C. Chen, G.L. Ma, *J. Mater. Sci.* 43 (2008) 5109–5114.
- [13] I.A. Amar, R. Lan, C.T. Petit, V. Arrighi, S.W. Tao, *Solid State Ionics* 182 (2011) 133–138.
- [14] I.A. Amar, C.T. Petit, L. Zhang, R. Lan, P.J. Skabar, S.W. Tao, *Solid State Ionics* 201 (2011) 94–100.
- [15] G. Marnellos, S. Zisekas, M. Stoukides, *J. Catal.* 193 (2000) 80–87.
- [16] G.J. Janz, M.R. Lorenz, *J. Chem. Eng. Data* 6 (1961) 321–323.
- [17] R.J. Olivares, C. Chen, S. Wright, *J. Solar Energy Eng. -Trans. ASME* 134 (2012).
- [18] C. Xia, L. Li, Y. Tian, Q. Liu, Y. Zhao, L. Jia, Y. Li, *J. Power Sources* 188 (2009) 156–162.
- [19] L. Fan, C. Wang, M. Chen, B. Zhu, *J. Power Sources* 234 (2013) 154–174.
- [20] L. Zhang, R. Lan, A. Kraft, S.W. Tao, *Electrochem. Commun.* 13 (2011) 582–585.
- [21] L. Zhang, R. Lan, X. Xu, S.W. Tao, Y. Jiang, A. Kraft, *J. Power Sources* 194 (2009) 967–971.
- [22] I.A. Amar, R. Lan, C.T. Petit, S.W. Tao, *J. Solid State Electrochem.* 15 (2011) 1845–1860.
- [23] W. Rarog-Pilecka, E. Miskiewicz, L. Kepinski, Z. Kaszkur, K. Kielar, Z. Kowalczyk, *J. Catal.* 249 (2007) 24–33.
- [24] R.D. Shannon, *Acta Cryst.* A32 (1976) 751–767.
- [25] M. Stange, J. Linden, A. Kjekshus, N. Binsted, M.T. Weller, B.C. Hauback, H. Fjellvag, *J. Solid State Chem.* 173 (2003) 148–163.
- [26] G. King, P.M. Woodward, *J. Mater. Chem.* 20 (2010) 5785–5796.
- [27] T. Sugahara, M. Ohtaki, *Appl. Phys. Lett.* 99 (2011) 062107.
- [28] W. Wang, X. Cao, W. Gao, F. Zhang, H. Wang, G. Ma, *J. Membr. Sci.* 360 (2010) 397–403.
- [29] E. Perman, G. Atkinson, *Proceedings of the Royal Society, London*, 74, 1904, pp. 110–117.
- [30] D.A. Cooper, E.B. Ljungstrom, *Energy Fuels* 2 (1988) 716–719.
- [31] A. Scheibe, U. Lins, R. Imbihl, *Surf. Sci.* 577 (2005) 1–14.
- [32] P.A. Webley, J.W. Tester, H.R. Holgate, *Ind. Eng. Chem. Res.* 30 (1991) 1745–1754.
- [33] A. Boisen, S. Dahl, J.K. Norskov, C.H. Christensen, *J. Catal.* 230 (2005) 309–312.
- [34] C.N. Satterfield, *Heterogeneous Catalysis in Practice*, McGraw-Hill, New York, 1980, pp. 301–308.